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Direct measurement of the thermomechanical Lehmann coefficient in a compensated cholesteric liquid crystal

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Abstract – The thermomechanical Lehmann coefficient ν is directly measured as a function of temperature in a compensated cholesteric liquid crystal. The method consists of observing the continuous rotation of the director in samples treated for planar sliding anchoring when a temperature gradient is applied perpendicularly to the director. The main result is that there is no relationship between the Lehmann coefficient and the equilibrium twist q. In particular, we confirm that ν does not vanish at the compensation temperature at which $q = 0$, in agreement with previous static measurements of Éber and Jánossy (*Mol. Cryst. Liq. Cryst.*, **72** (1982) 233) and of ourselves (*Europhys. Lett.*, **80** (2007) 26001). In addition, the sign of the Lehmann coefficient is determined by observing between crossed polarizers the sense of rotation of the extinction branches of the disclination lines.

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Introduction. – In a nematic liquid crystal, the rod-like molecules tend to align along a single direction characterized by a unit vector $\vec{n}$ called the director (with $\vec{n} \Leftrightarrow -\vec{n}$). If one adds chiral molecules to a nematic phase, one obtains a cholesteric phase in which the director rotates around a space direction called the helical axis. In practice, there is no obvious relationship between the molecular chirality and the value of the equilibrium twist of the phase q [1]. For this reason, there exist materials in which q can vanish and change sign at a given temperature called the compensation temperature T_c.

Chirality can also lead to strange phenomenon in hydrodynamics. One of the most spectacular was revealed in 1900 by Otto Lehmann who observed that the texture of particular cholesteric droplets sandwiched between two glass plates could be put into motion when heated from below [2,3]. This phenomenon was explained qualitatively 68 years later by Leslie [4], who showed that the absence of inversion symmetry in a cholesteric phase allows the existence of an internal torque driven by a temperature gradient, of expression [5,6]

$$\vec{\Gamma}_{\text{Lehmann}} = -\nu \vec{G}_\perp, \tag{1}$$

where $\vec{G}_\perp = (\vec{n} \times \vec{G}) \times \vec{n}$ is the component of the temperature gradient $\vec{G} = \vec{\nabla} T$ perpendicular to $\vec{n}$ and ν the thermomechanical Lehmann coefficient.

Suppose now that the director can freely rotate at the boundaries limiting the sample. It comes immediately from the previous equation that the helix of a cholesteric liquid crystal must rotate at a constant angular velocity ω when it is subjected to a temperature gradient parallel to its axis. This velocity can be easily obtained by equilibrating the Lehmann and viscous torques and reads

$$\omega = -\nu G/\gamma_1, \tag{2}$$

where γ_1 is the rotational viscosity.

Recently, we reported the first preliminary observation of the continuous Lehmann rotation of the cholesteric helix under the action of a temperature gradient [7,8]. This experiment was made possible thanks to the development of a new surface treatment allowing for planar and sliding anchoring of the molecules at the glass plates limiting the sample [9]. On the other hand, it was just a feasibility experiment because of the lack of an appropriate setup to impose a controlled temperature gradient.

In this article, we fill this gap and we perform the first direct and quantitative measurements of the Lehmann coefficient in a compensated cholesteric as a function of

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temperature. We emphasize here that our measurements were done on both sides of the compensation point to settle the following question: does ν vanish and change sign at T_c as proposed by theorists [10,11] or can ν be different from 0 at T_c as found experimentally by Éber and Jánossy [12–14] and more recently by ourselves [7,8] by using a static measurement method (which only applies at T_c)?

Note for completeness that thermomechanical effects also exist in deformed nematics [15]. These effects are described by twelve thermomechanical coefficients ξ_i ($i = 1, \ldots, 12$), which, when divided by the typical length over which the director field is distorted, are formally equivalent to the Lehmann coefficient ν. In principle, these terms also exist in cholesterics when the helical structure is distorted, but we shall show later that their contribution is negligible in our experiment.

The plan of the article is the following. In the second section, we describe the sample preparation and our experimental setup. Then, we report our experimental results concerning the angular rotation velocity of the director as a function of the temperature and of the temperature gradient. In the next section, we show how to determine the sign of the Lehmann coefficient by observing the defects. The value of the Lehmann coefficient at the compensation temperature is then given and the importance of the nematic thermomechanical term is discussed. Finally, we draw conclusions in the last section.

Sample preparation and experimental setup. – Our liquid crystal is a mixture of 4-n-octyloxy-4′cyanobiphenyl (8OCB from Synthon Chemicals GmbH&Co) and of cholesteryl chloride (CC from Aldrich) in proportion 1 : 1 in weight with a compensation point at 58 °C and a clearing point at 66 °C. The 8OCB was purified by A. Żywocińsky and the CC was used without further purification. The mixture was filtered in the cholesteric phase through 0.2 μm nylon filter to remove dust particles. The sample is sandwiched between two glass plates. The bottom plate is covered with two ITO layers separated by a 2 mm wide central band. The two ITO layers are connected to a high-voltage power supply which allows us to impose a horizontal electric field to the liquid crystal within the gap separating the two ITO layers. The two plates are treated for planar sliding anchoring with the polymercaptan hardener of an epoxy glue (Structalit 7 from Eleco) [9]. The latter is dissolved in the 2-butanone (5% in mass) and spread by spin-coating on the plates. It is then held at 60 °C for one hour under vacuum in order to evaporate the solvent. Nickel wires of calibrated diameters are used as spacers to fix the sample thickness (25 μm in the present experiments). The liquid crystal is introduced by capillarity between the plates. Finally, the sample is sealed on the sides with the epoxy glue.

In order to impose a temperature gradient to the sample, a new setup was designed and constructed. It is shown in fig. 1. The sample is sandwiched between two transparent ovens regulated in temperature within ± 0.01 °C owing to two separated recirculating water baths. Two thin layers of glycerol are introduced between the sample and the ovens in order to enhance thermal contacts. With a home-made temperature sensor [9], we checked that the sample temperature was given by $(T_b + T_t)/2$ within ± 0.1 °C whatever the temperatures chosen for the top and bottom ovens (T_t and T_b, respectively). The two ovens are mounted on a precision XY stage of a polarizing Leica microscope allowing us to observe the complete sample. A video camera allows us to capture up to 30 images/s with a resolution of 1380×1024 pixels. In the following, we shall denote by ΔT the difference $T_t - T_b$. This quantity is directly proportional to the imposed temperature gradient G which will be evaluated later.

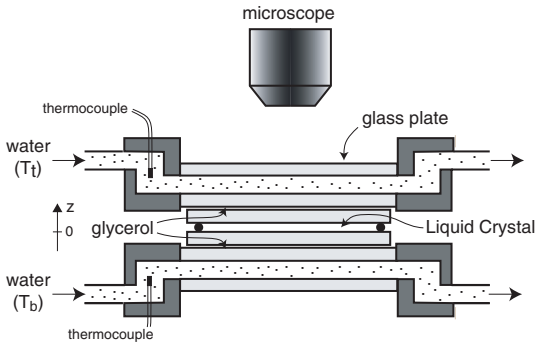


Fig. 1: Experimental setup. The z-axis is vertically oriented towards the top so that $G > 0$ when $T_t > T_b$.

Experimental results. – The first step was to determine precisely the compensation temperature T_c. As the latter is known within ± 0.5 °C, we started by fixing the temperature of the ovens at the presumed temperature. We then applied a large voltage (typically, 500 Vrms at frequency $f = 10$ kHz) between the two electrodes. Because the liquid crystal has a positive dielectric anisotropy ($\varepsilon_a \approx 5$ [16]), the director orients parallel to the electric field in the region lying between the two electrodes. As a consequence, the sample appears black in this region between crossed polarizer and analyzer when the polarizer is either parallel or perpendicular to the electric field. We then switch off the voltage. If the temperature is different from T_c the director field winds again and the extinction disappears. On the other hand, the extinction persists if the temperature is equal to T_c as the sample is "nematic" at this temperature. Thus, one can determine T_c by looking for the temperature at which the extinction persists. In our experiments, we found $T_c = 57.8 \pm 0.1$ °C.

Once T_c was determined, we started by increasing the temperature difference between the two ovens while maintaining the sample temperature equal to T_c. Doing this we observed that the transmitted intensity between

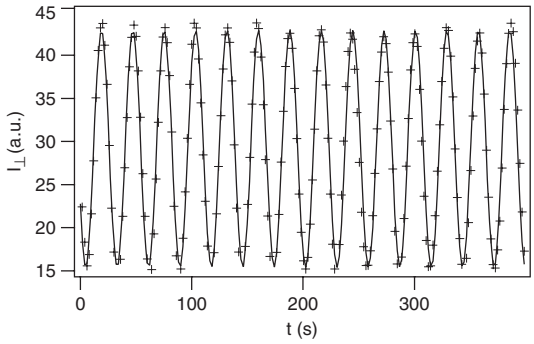


Fig. 2: Intensity measured between crossed polarizers as a function of time after the electric field has been removed. The solid line is the fit to a sine function. $T = T_c$ and $\Delta T = 40\,^{\circ}\mathrm{C}$.

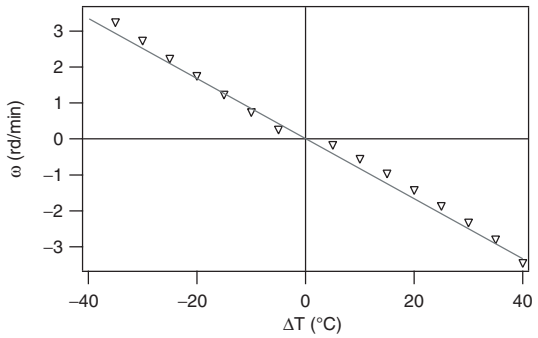


Fig. 3: Angular rotation velocity as a function of the temperature difference. $T = T_c$.

crossed polarizer and analyzer began to oscillate in time immediately after the field was removed. This oscillation is clearly due to the Lehmann rotation of the director. Note that the intensity oscillates at the angular velocity 4ω because it passes through a minimum each time the director is parallel or perpendicular to the polarizer. Figure 2 shows the intensity as a function of time. As expected, it is very well fitted with a sine function, which is the sign that the director regularly rotates on the two glass plates.

In fig. 3 we reported the director angular velocity ω as a function of the temperature difference ΔT. This graph shows that the angular velocity (the sign of which can be determined by observing the sense of rotation of the extinction branches of the defects as we shall show in the next section) is proportional to ΔT (and, thus, to the temperature gradient G) in agreement with eq. (2).

Finally, we measured ω as a function of the sample temperature $T = (T_b + T_t)/2$ while maintaining ΔT constant. Our results are reported in fig. 4. They show unambiguously that the angular velocity and, thus, the Lehmann coefficient ν, do not vanish at T_c, contrary to the equilibrium twist q.

Sign of the Lehmann coefficient. – The intensity curves as a function of time like that shown in fig. 2 only give the absolute value of ω. A method to determine the sign of ω consists of observing between crossed polarizers

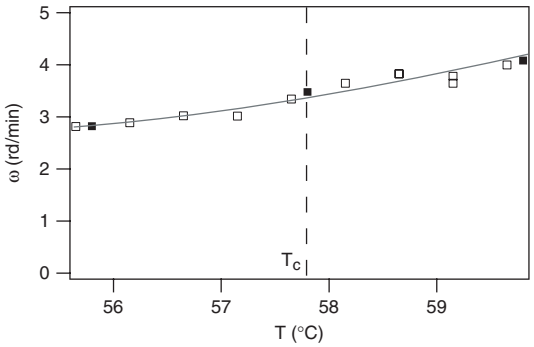


Fig. 4: Angular velocity as a function of the sample temperature for a fixed temperature difference $\Delta T = -40\,^{\circ}\mathrm{C}$. The open and filled squares correspond to two different samples of thickness $d = 25\,\mu$m.

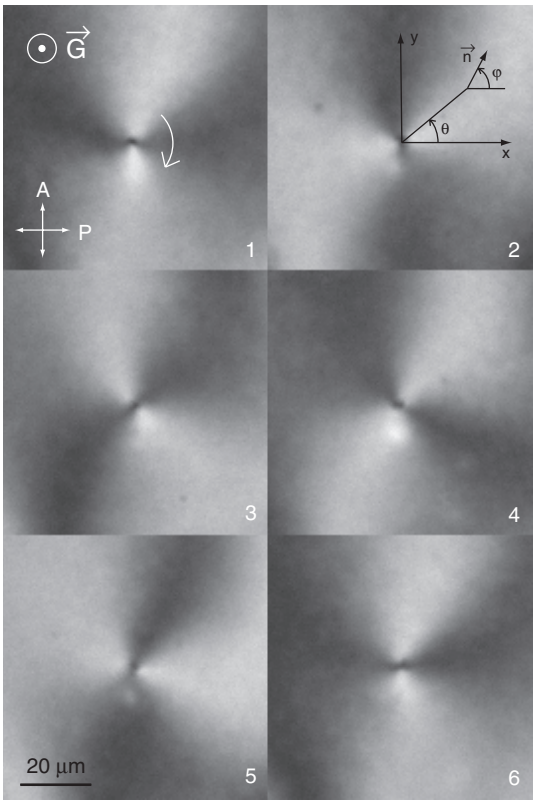


Fig. 5: The two extinction branches of a $-1/2$ disclination line rotate clockwise when the temperature gradient is positive. The interval time between two photographs is 11 s. $T = T_c$ and $\Delta T = 38.5\,^{\circ}\mathrm{C}$.

the sense of rotation of the extinction branches of the wedge disclination lines. The latter form in large number when the sample is cooled down from the isotropic liquid. In practice, most of the lines are of topological strength $m = \pm 1/2$. Such a defect is shown in fig. 5. In this example, $m = -1/2$ because the branches turn in the opposite direction of the polarizers. In order to determine at which angular velocity the branches must rotate under the action of the Lehmann effect, let us give the expression of the angle φ between the director and the x-axis around the

core of a disclination line. Because the director rotates with the angular velocity ω, one has for a disclination line of strength m situated at the origin

$$\varphi = m\theta + \omega t, \tag{3}$$

where θ is the polar angle (fig. 5). If the polarizer (respectively, the analyzer) is parallel to the x-axis (respectively, the y-axis), there is extinction at places where $\varphi = 0$ and $\pi/2$. This defines the equation of the two extinction branches

$$\theta = -\frac{\omega}{m}t \quad \text{and} \quad \theta = \frac{\pi}{2m} - \frac{\omega}{m}t. \tag{4}$$

These equations show that the branches of a $-1/2$ (respectively, $+1/2$) disclination line must rotate with the angular velocity 2ω (respectively, -2ω).

Let us now return to fig. 5 showing a $-1/2$ defect. In this example, $T = T_c$, $G > 0$, and the two extinction branches rotate clockwise which means that $\omega < 0$. From this observation and according to eq. (2) we deduce that $\nu > 0$ at T_c. We checked that the same result holds in the whole investigated range of temperature (about 2 °C on both sides of T_c).

Value of the Lehmann coefficient at the compensation temperature. – In practice, eq. (2) must be corrected because the director does not slide freely on the polymercaptan layers, but experiences a viscous surface torque of expression $\Gamma_S = -\gamma_S \vec{n} \times \frac{\partial \vec{n}}{\partial t}$ [9]. In this condition, γ_1 must be replaced in this equation with a larger effective viscosity γ_1^* which takes into account the dissipation at the surfaces. To show this result and explicitly calculate γ_1^*, let us write the basic equations of the problem.

Let φ be the angle between the director and the x-axis parallel to the plates. In the bulk, the torque equation reads

$$K_2 \frac{\partial^2 \varphi}{\partial z^2} - K_2 \frac{\partial q}{\partial z} = \nu G + \gamma_1 \frac{\partial \varphi}{\partial t}, \tag{5}$$

where K_2 is the twist constant and q the equilibrium twist. Note that in this equation, we took into account the temperature variation of q along z but neglected the K_2 variation. This is justified around T_c because only q is strongly dependent on the temperature.

At the bottom plate, the surface torque equation reads

$$-K_2 \left(\frac{\partial \varphi}{\partial z} - q(0) \right) + \gamma_S \frac{\partial \varphi}{\partial t} = 0 \quad \text{at} \quad z = 0, \tag{6}$$

while at the top plate it reads

$$+K_2 \left(\frac{\partial \varphi}{\partial z} - q(d) \right) + \gamma_S \frac{\partial \varphi}{\partial t} = 0 \quad \text{at} \quad z = d. \tag{7}$$

To solve these equations, we need to know the $q(T)$ variation. In previous works [7,8], we showed that q changes linearly with temperature around T_c within an excellent approximation. This allowed us to write that $\frac{\partial q}{\partial z} = \frac{\mathrm{d}q}{\mathrm{d}T} G$ in eq. (5) and that $q(d) = q(0) + \frac{\mathrm{d}q}{\mathrm{d}T} G d$ in eq. (7) where $\frac{\mathrm{d}q}{\mathrm{d}T}$ is a constant. In this condition, the solution can be written in the form $az + bz^2 + \omega t$, where a and b are two constants describing the spatial distortions of the helix, while ω is its angular velocity. A straightforward calculation yields

$$\omega = -\frac{\nu}{\gamma_1^*} G, \tag{8}$$

where $\gamma_1^* + \gamma_1 + 2\gamma_S/d = 0$ is an effective viscosity larger than the bulk viscosity γ_1. This equation generalizes eq. (2) as it includes the surface viscous dissipation.

It turns out that γ_1 and γ_S were measured in a previous work at the compensation temperature: $\gamma_1 = 0.075\,\mathrm{Pa\,s}$ and $\gamma_S = 3.2 \times 10^{-7}\,\mathrm{Pa\,s\,m}$ [9]. As a consequence, the only quantity which remains to determine to estimate the Lehmann coefficient is the temperature gradient G across the liquid crystal layer. In practice, the glass plates are much thicker than the glycerol and liquid crystal layers. In these conditions, we can neglect in a first approximation the temperature variations across them, which gives

$$G \approx \frac{\Delta T}{4e} \frac{\kappa_g}{\kappa_{LC}}, \tag{9}$$

where e is the thickness of a glass plate (1.1 mm) and κ_g and κ_{LC} the thermal conductivities of the glass and of the liquid crystal, respectively.

To measure the ratio κ_g/κ_{LC} we replaced the upper glycerol layer with a thin layer of pure 8OCB. Our material has a nematic-to-smectic A phase transition at temperature $T_{NA} = 66.2\,^\circ\mathrm{C}$. As this transition is easy to detect under the microscope, it can therefore be used to fix a temperature. To measure the conductivity ratio, we thus changed the temperatures T_b and T_t while maintaining the temperature of the 8OCB layer exactly at T_{NA}. In this condition, it can be shown that T_b and T_t must satisfy the following equation:

$$T_b = \frac{4x+1}{x} T_{NA} - \frac{3x+1}{x} T_t, \tag{10}$$

where $x = \frac{e}{d} \frac{\kappa_{LC}}{\kappa_g}$. Thus, measuring T_b as a function of T_t allows us, in principle, to measure the ratio κ_g/κ_{LC}. To increase the sensibility of the measurement, x must be as small as possible. For this reason, we used a thick sample of the 8OCB-CC mixture: $d = 550\,\mu\mathrm{m}$. Our experimental results are shown in fig. 6. The best fit to eq. (10) gives $x = 0.29$ from which we calculate $\kappa_g/\kappa_{LC} \approx 7$.

We can now calculate the value of ν at T_c from eqs. (8), (9) and knowing that $\omega \approx 3.4\,\mathrm{rad/min}$ when $\Delta T = 40\,^\circ\mathrm{C}$ and by using the previous values of γ_1, γ_S and of the ratio κ_g/κ_{LC}. This gives

$$\nu \approx 1 \times 10^{-7}\,\mathrm{kg\,K^{-1}\,s^{-2}}.$$

This value is twice as small as the value we found before by a static method [7,8]. This difference can come from the fact that we overestimate the temperature gradient by neglecting the thermal losses as well as

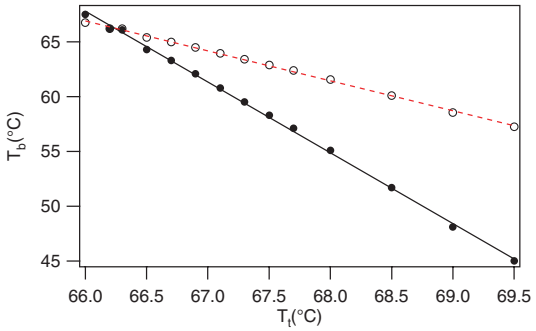


Fig. 6: Bottom temperature as a function of the upper temperature and the best fit to eq. (10) (solid line). The open circles give the temperature in the middle of the liquid crystal layer.

the influence of the two glycerol layers. In addition, the ratio of the two conductivities has been measured at a larger temperature than T_c in a disoriented sample which generates a supplementary error. Finally, it is possible that we underestimate γ_S and, thus, the effective viscosity γ_1^*, because we did not use the same glue sample as in ref. [9]. For these reasons, the value of ν given before must be regarded as giving only a good order of magnitude.

Before concluding, we return to the nematic thermomechanical terms [15] which we mentioned in the introduction and neglected so far. This is not strictly correct because the helix deforms when it rotates under the action of the temperature gradient. This effect introduces in the r.h.s. of eq. (5) an additional term of the type $\xi(\frac{\partial\varphi}{\partial z} - q)G$. Taking into account this term is possible but leads to a non-linear relationship between the angular velocity ω and the temperature gradient G. This is not observed within experimental errors (see fig. 3), which suggests that this term is indeed negligible in our experiments. More precisely, it can be shown from eq. (5) that this term can be neglected if $\xi < \frac{K_2}{dG}$. This inequality shows that the smaller the temperature gradient or the thickness, the weaker the effect of the thermomechanical nematic term. In our experiment, $d = 25\,\mu$m and the maximum temperature gradient used was $G \approx 6 \times 10^4\,^\circ$C/m. Knowing that $K_2 \approx 3 \times 10^{-12}$ N [7,8] at T_c, we estimate that $\xi < 3 \times 10^{-12}\,\mathrm{kg\,m\,K^{-1}s^{-2}}$ in our CC-8OCB mixture. This conclusion is not incompatible with a previous estimate of a similar coefficient in the liquid crystal 5CB (pentylcyanobiphenyl) in which $\xi \sim 10^{-12}\,\mathrm{kg\,m\,K^{-1}s^{-2}}$ [17].

Conclusions. – To summarize, our experiment shows directly for the first time the continuous Lehmann rotation of a cholesteric helix when it is subjected to a temperature gradient. Owing to a new setup, we were able to measure its angular velocity and to show that it is proportional to the temperature gradient in agreement with the theory. We also determined the absolute value of the Lehmann coefficient ν and its sign by observing the sense of rotation of the extinction branches of the disclination lines. More importantly, we found that the Lehmann coefficient remains positive on both sides of the compensation point and so does not vanish nor changes sign at this point, contrary to the equilibrium twist q. This result agrees with static measurements of ν at T_c [7,8,12–14] and contradicts the usual idea according to which ν must be proportional to q [10,11]. The reason for this counterintuitive result is that the cholesteric phase has never inversion symmetry, even at T_c when it is unwound and has a nematic-like structure, because of the chirality of the molecules. It is for similar symmetry reason that a chiral isotropic liquid (as, for instance, a solution of saccharose in water) has rotatory power. As a consequence, there is no obvious relationship between the Lehmann coefficient and the equilibrium twist. From this point of view it would be interesting to investigate how these two quantities change with the concentration and the nature of the chiral molecules. Such experiments are now in progress. Finally, note that nematic thermomechanical effects are too small to be detected in this experiment.

* * *

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